

Appl. No.: 10/798,164
Amendment Dated: September 12, 2006
Reply to Office Action of March 13, 2006

REMARKS/ARGUMENTS

Claims 2-4, 6-14, 17, 23, 32-42, 49 and 50 have been objected to because of informalities set forth on page 3 of the Office Action.

It is respectfully submitted that the claims as now amended have overcome all of the informal objections. Applicant regrets any inconvenience.

Claims 2-4, 6-14, 17, 23, 32-42 and 49 stand rejected under 112, second paragraph. The Examiner with respect to this rejection has interpreted Claim 2 to be dependent upon Claim 50 which is correct with the exception that Claim 50 has now been cancelled such that Claim 2 is dependent upon new Claim 51.

Turning to the art rejections, Claims 2-4, 6-14, 17, 23, 32-42, 49 and 50 stand rejected under 35 U.S.C. 102(a) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over DE 19855080. Enclosed herewith is a translation of DE 19855080. It is respectfully submitted that with the submission of the translation of this reference, this rejection has been overcome since it was filed less than one year before the relevant priority date and was published after the priority date.

Claims 2-4, 6-14, 17, 23, 32-42, 49 and 50 stand rejected under U.S.C. 102(b) as anticipated or in the alternative under U.S.C. 103(a) as obvious over DE 19622612. The rejection is respectfully traversed. At the outset, enclosed herewith is a translation of DE 19622612. The Examiner contends that the '612 reference teaches an active care ingredient in skin care and hair treatment

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agents that is a mixture of a diacylalkenyldiaminodicarboxylic acid and an oil, fat, or wax. The Examiner also contends that the '080 reference teaches the same surfactants as recited by Formula B.III of the instant claims. The Examiner thus concludes that the '612 reference would inherently disclose compositions containing the same components in the same amounts having the same properties as recited by the present claims, i.e., that it has sufficient specificity to constitute anticipation. In the alternative, the Examiner's position is that if the teachings of the '612 reference are insufficient for anticipation purposes that it would have been obvious to the skilled artisan to arrive at Applicants' claimed compositions in part because the '080 reference teaches that the amounts and types of required components added to the composition may be varied. At the outset, as noted above, the '080 reference is not prior art.

While the Examiner is correct that the '612 reference does mention gemini surfactants of which some may fall within Formula B.III, the '612 reference does not teach that at least two of the co-amphiphiles as set forth in new Claim 51 form part of the composition. The '612 reference under the heading "Surfactants" starting on the bottom of page 4, does mention polyol fatty acid esters, sugar esters and sorbitan esters but clearly does not teach to use at least two in one composition. Stated differently, the '612 reference does not teach to use two co-amphiphiles as set forth in new Claim 51.

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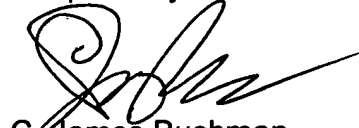
Additionally, as to the '080 reference, while it does disclose on page 4 "Suitable waxes, fats and oils are, for example, natural fats and oils, mono-, di- and triglycerides of saturated and unsaturated fatty acids . . . ". Alkylglycosides as well as polyol esters are mentioned on page 8 as consistency regulators only. The non-ionic surfactants mentioned in the '080 reference are different from the co-amphiphiles claimed in Claim 51 albeit that the '080 reference may disclose propylene glycol C₆-C₁₂ esters.

In any event, since the '080 reference is not prior art as to the present claims, it cannot be combined with the teachings of the '612 reference. That being the case and since neither the '612 reference or the '080 reference, even assuming it was prior art, teach or suggest the use of at least two of the co-amphiphiles set forth in Claim 51, it is respectfully submitted that Claim 51 and claims dependent thereon are patentable over the '080 and '612 references.

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In view of the foregoing amendments and remarks, Applicant respectfully submits that all claims are in condition for allowance which is hereby earnestly solicited and respectfully requested.

Respectfully submitted,



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DE 198 55 080 A 1

Application disclosed with applicant's consent pursuant to § 31 Sec. 2 Clause 1 PatG [Patent Act].

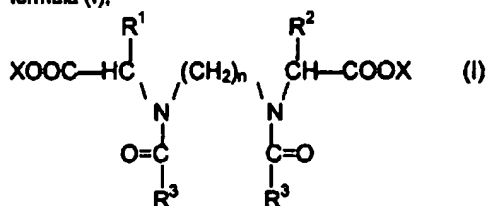
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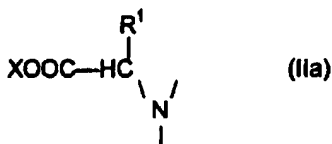
The following information is taken from the documents submitted by the applicant

(54) Treatment agents for skin and hair care

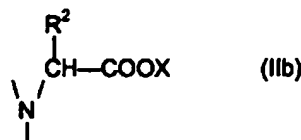
(57) The present invention relates to skin and hair treatment agents which contain as active care substances a mixture of at least one diacyl-alkenyldiaminodicarboxylic acid according to formula (I),



where the units



and



stand in each instance, independently of one another, for an α -aminocarboxylic acid residue, R^2 stands for a saturated, mono- or polyunsaturated, branched or unbranched C_{1-} to C_{21} -alkyl radical, n stands for an integer from 1 to 20 and X stands for hydrogen or for an equivalent of an alkali, alkaline earth, ammonium, alkylammonium, hydroxyalkylammonium and/or glucammonium cation, and which contain at least one oil, fat and/or wax. These agents are distinguished by an exceptional mildness and excellent skin and hair care results.

DE 196 22 612 C 1

Description

The invention relates to treatment agents for skin and hair care which contain as active care substances a mixture of at least one diacyl-alkenyldiaminodicarboxylic acid as well as at least one oil, fat and/or wax, and to the use of mixtures of this type.

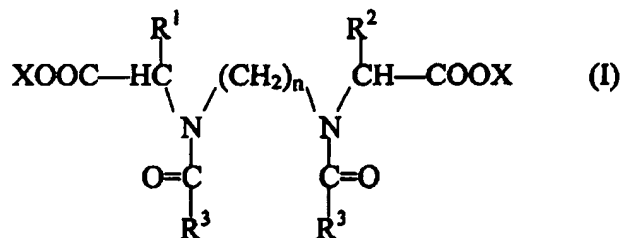
Surfactant-containing preparations which are used for the cleaning and care of skin or hair can have the disadvantage that application thereof leads to severe degreasing of the skin and/or to an undesired swelling of the keratin layer. The condition of the skin then becomes dry, brittle or rough, thereby causing an unpleasant skin sensation. In addition, the structure of the hair may also be negatively affected if hair colouring or waving agents are applied that contain oxidative substances such as hydrogen peroxide or reductive substances such as thioglycolic acid. This results in deterioration of wet combability or also to an unsatisfying feel. Care components, usually quaternized polymers, are therefore added to hair care agents which contain surfactants. The use of these quaternized polymers cannot be entirely satisfactory, however, as the hair, especially in dry air, may present an unfavourable electrostatic charge when being dressed. In addition, the formulations with quaternized polymers tend to thicken when stored for longer periods, which is troublesome particularly in the case of hair colouring creams. For this reason, oleic acid soaps in combination with fatty alcohols have also been proposed as care components in hair colorants. But even this mixture is not entirely satisfactory, as in the presence of hard water the soaps form undesired insoluble calcium soaps. In addition, large quantities of lower alcohols are required to improve rheological properties, but this is undesirable in view of skin compatibility. The goal of our research has been to overcome the disadvantages described above.

Surprisingly, it was discovered that a mixture of diacyl-alkenyldiaminodicarboxylic acids with at least one oil, fat or wax exhibits, with regard to the skin and hair care properties thereof, a synergistic effect far in excess of a purely additive effect of the individual components of the mixture.

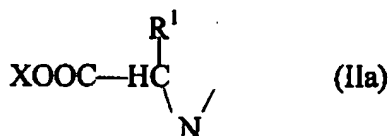
The present invention therefore relates to treatment agents for skin and hair care which contain as active care substances

- (A) a mixture of at least one diacyl-alkenyldiaminodicarboxylic acid and
- (B) at least one oil, fat and/or wax.

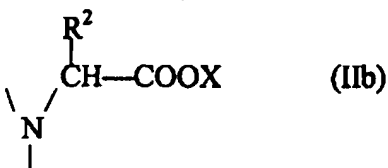
Diacyl-alkenyldiaminodicarboxylic acids according to the invention are compounds of formula (I)



where the units



and



stand in each instance, independently of one another, for an α -aminocarboxylic acid residue, R^3 stands for a saturated, mono- or polyunsaturated, branched or unbranched C_{1-} to C_{21} -alkyl radical, and n stands for an integer from 1 to 20. The diacyl-alkenyldiaminodicarboxylic acids can be used in the agents according to the invention as, depending on the pH value, free acids (X standing for hydrogen) or in the form of the salts thereof (X corresponding to an equivalent of an alkali, alkaline earth, ammonium, alkylammonium, hydroxyalkylammonium and/or glucammonium cation).

α -aminocarboxylic acids are to be understood according to the invention as the naturally occurring L- α -aminocarboxylic acids, for example L-asparaginic acids, L-glutamic acids, L-lysine, L-arginine, L-histidine, L-citrulline, L-homocysteine, L-homoserine, hydroxyproline, hydroxylysine, L-ornithine, sarcosine, L-alanine, L-valine, L-leucine, L-isoleucine, L-proline, L-tryptophan, L-phenylalanine, L-methionine, L-serine, L-tyrosine, L-threonine, L-cysteine, L-asparagine, L-glutamine and preferably glycine. Also counted according to the invention among the α -aminocarboxylic acids, in addition to the naturally occurring L- α -aminocarboxylic acids, are the corresponding D- α -amino acids, or other synthetic α -aminocarboxylic acids where R^1 or R^2 stand for hydrogen or an alkyl or aryl radical having in each instance from 1 to 20 carbon atoms and which may carry heteroatoms such as N, O, or S also in the form of other functional groups.

If the amino acid residues in formula (I) carry other acid functions, these may be present, depending on the pH value, both in protonated form and in the form of the salts thereof with an alkali, alkaline earth, ammonium, alkylammonium, hydroxyalkylammonium and/or glucammonium cation.

Compounds of formula (I) and their preparation have already been described in DE-C1-196 22 612 and in US 5,756,784. The compounds also described as gemini surfactants are distinguished by their good surfactant properties and are also very mild. There is, however, no reference to be found in the publications to a synergistic care effect in combination with oils, fats or waxes.

Particularly preferred components (A) are compounds of formula (I) where R^1 and R^2 stand for hydrogen.

In addition, preference may be given according to the invention to compounds of formula (I) where R^3 stands for a C_8 - to C_{18} -alkyl radical, in particular for a C_{11} -alkyl radical.

Dilauroyl ethylenediamine diacetic acid and the salts thereof are compounds of formula (I) to which very particular preference is given.

Suitable waxes, fats and oils are, for example, natural fats and oils, mono-, di- and triglycerides of saturated and unsaturated fatty acids, ethylene glycol esters of fatty acids, fatty acids, low ethoxylated fatty acids, fatty alcohols, low ethoxylated fatty alcohols, cholesterol and low ethoxylated cholesterols, but also synthetic products such as, for example, polydialkyl- or polyalkylphenylsiloxanes. Low ethoxylated compounds are to be understood according to the invention as those with a degree of ethoxylation less than 5.

Fatty acids, low ethoxylated fatty acids, fatty alcohols and low ethoxylated fatty alcohols have proven to be especially effective. Corresponding mixtures can also be used as components (B).

Fatty acids having from 6 to 22 carbon atoms and mixtures thereof are especially suitable as fatty acids. Preference is given to fatty acids having from 12 to 22 carbon atoms and mixtures thereof. Suitable fatty acids are in particular the saturated fatty acids, selected from the group formed by capric, lauric, myristic, palmitic, stearic, isostearic and behenic acid. Particularly suitable are lauric, myristic and isostearic acid.

Mixtures with fatty alcohols, in particular those having from 6 to 22 carbon atoms, have particularly good care properties for purposes of the invention. Preference is given to fatty alcohols having from 12 to 22 carbon atoms. Suitable fatty alcohols are saturated fatty alcohols such as caprylic, pelargonic, capric, lauryl, myristyl, cetyl, stearyl, arachidyl and behenyl alcohol, and also mixtures thereof.

Other examples of components (B) are tallow fatty alcohols, coconut fatty alcohol, jojoba oil, paraffin oil and polydimethylsiloxanes.

Preferred components (B) are long-chain fatty alcohols such as cetearyl alcohol and stearyl alcohol, mixtures thereof, and natural fatty alcohol mixtures with a high content of these components.

The use of water-insoluble oils, fats or waxes can, according to the invention, be preferred. To be understood for purposes of the application as water-insoluble are those substances whose solubility in water at 20°C is 1 g/l or less. Substances with a solubility of 0.1 g/l and less are preferred.

The ratio in which the components (A) and (B) are present in the agent according to the invention may vary within wide ranges. Particularly good care properties can be achieved if the components (A) are present in relation to components (B) in a ratio of from 20:1 to 1:10 by weight.

An embodiment of the present invention relates to aqueous treatment agents for skin care that contain as active care substances the mixture described above. Aqueous treatment agents for skin care are, for example, hand and body washing lotions, shower gels, foam baths and rinsable skin care emulsions. In aqueous skin treatment agents of this type, the care mixture described above is contained preferably in quantities of from 1 to 30% by weight, based on the skin treatment agent.

Other components may be, depending on the application, anionic, cationic, nonionogenic or ampholytic surfactants, fragrances, essential oils, antimicrobial substances and preservatives, thickeners, complexing agents, opacifiers and pearlizers, pH regulators, and dyes, which are used in the quantities familiar to the specialist. Particularly good care properties and an especially pleasant skin sensation are achieved if the pH value of the aqueous skin treatment agent is less than 9, particularly if it is between 4 and 7. This can

occur in the usual manner through the addition of corresponding pH adjusting agents such as triethanolamine or citric acid.

Another embodiment of the present invention relates to treatment agents for hair care and comprises both agents that remain on the hair and those agents that, after an exposure time of from a few seconds to minutes, are rinsed out again. Examples of hair treatment agents according to the invention are shampoos, rinses, restorers, conditioners, tinting agents, colorants, perming agents, fixatives and blow dries. The care mixtures are contained in these hair treatment agents in quantities of from 5 to 40% by weight, based on the hair treatment agent.

The agents used according to the invention can be formulated, for example, as aqueous, alcoholic or aqueous alcoholic solutions, creams, gels or emulsions. In the simplest case, a solution of the obligatory components according to patent claim in water or aqueous alcohol suffices as a carrier. All cosmetic carriers in their typical composition for known hair care agents are, however, suitable for the combination of active substances according to the invention.

Aqueous alcoholic solutions are to be understood for purposes of the present invention as aqueous solutions containing from 3 to 70% by weight of a C₁- to C₄-alcohol, in particular ethanol or isopropanol.

It has been found that other components determined practically independently of the type of hair treatment agent particularly advantageously complement the effect which the combination of active substances has.

The nonionogenic surfactants represent a class of such components. Such compounds are, for example,

- addition products of from 1 to 30 mol of ethylene oxide and/or from 0 to 5 mol of propylene oxide with linear fatty alcohols having from 8 to 22 carbon atoms, with fatty acids having from 12 to 22 carbon atoms and with alkyl phenols having from 8 to 15 carbon atoms in the alkyl group;
- C₁₂₋₂₂-fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide with glycerol;
- addition products of from 1 to 30 mol of ethylene oxide and/or from 0 to 5 mol of propylene oxide with fatty acid esters, for example methyl esters, or esterification products of fatty acids with ethoxylated and/or propoxylated alcohols,
- C₈-C₂₂-alkyl mono- and oligoglycosides and ethoxylated analogs thereof, and
- addition products of from 5 to 60 mol of ethylene oxide with castor oil and hydrogenated castor oil.

These compounds with alkyl groups can in each instance be homogeneous substances. Normally, however, preference is given in the preparation of these substances to starting with raw materials of plant or animal origin, so that mixtures of substances are obtained which have different alkyl chain lengths depending on the raw material in each instance.

In the case of the nonionogenic surfactants, which represent the addition products of ethylene and/or propylene oxide with fatty alcohols or derivatives of these addition products, both products with a "normal" homolog distribution and those with a narrowed homolog distribution can be used. "Normal" homolog distribution is to be understood as the mixtures of homologs that are obtained through the reaction of fatty alcohols and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. Narrowed homolog distributions, on the other hand, are obtained when, for

example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, or alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. Preference may be given to the use of products with narrowed homolog distribution.

Alkyl polyglycosides according to the formula $RO-(Z)_x$, where R stands for an alkyl radical having from 8 to 22 carbon atoms, Z stands for a mono- or oligosaccharide and x stands for a number from 1.1 to 5, are particularly preferred nonionogenic surfactants. These compounds are characterized by the following parameters.

The alkyl radical R contains from 8 to 22 carbon atoms and can be either linear or branched. Preference is given to primary linear and 2-methyl-branched aliphatic residues. Examples of such alkyl radicals are 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl. Particular preference is given to 1-octyl, 1-decyl, 1-lauryl, 1-myristyl. When what are known as "oxo alcohols" are used as starting materials, compounds with an uneven number of carbon atoms in the alkyl chain predominate.

The alkyl glycosides which can be used according to the invention can contain only one certain alkyl radical R. Usually, however, these compounds are prepared starting from natural fats and oils or mineral oils. In this case, mixtures corresponding to the starting compounds or corresponding to the respective work-up of these compounds are present as alkyl radicals R.

Particular preference is given to those alkylpolyglycosides in which R consists

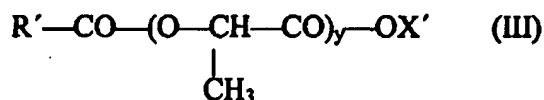
- essentially of C_8 - and C_{10} -alkyl groups,
- essentially of C_{12} - and C_{14} -alkyl groups,
- essentially of C_8 - to C_{16} -alkyl groups,
- essentially of C_{12} - to C_{16} -alkyl groups.

Any desired mono- or oligosaccharide can be used as a sugar building block Z. Usually, sugars with 5 or 6 carbon atoms and the corresponding oligosaccharides are used. Such sugars are, for example, glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. Preferred sugar building blocks are glucose, fructose, galactose, arabinose and sucrose; glucose is particularly preferred.

The alkyl polyglycosides which can be used according to the invention contain, on average, 1.1 to 5 sugar units. Alkyl glycosides with x values of from 1.3 to 2 are preferred. Very particular preference is given to alkyl glycosides in which x is from 1.4 to 1.6.

Hair treatment agents which contain as a hair fixing component, in addition to the combination of active substances according to the invention, acyl lactylate and/or water-soluble starch have likewise proven to be particularly advantageous.

Suitable acyl lactylates have the general formula (III),



where R' stands for a linear or branched, saturated or unsaturated alkyl or alkenyl group having from 6 to 22 carbon atoms, X' for hydrogen, an alkali, ammonium or alkanolammonium cation or an alkaline reacting amino acid, and y for a number from 1 to 5.

Particular preference is given to acyl lactylates in which R' stands for an alkyl group, particularly one which is saturated, linear or methyl-branched, having from 12 to 18 carbon atoms and y stands for a number from 1 to 3.

These acyl lactylates are commercially available under the trademark Pationic®.

A sodium isostearoyl lactylate marketed under the name Pationic®ISL is a particularly preferred acyl lactylate.

The hair treatment agents according to the invention contain the hair-fixing agents preferably in a quantity of from 0.1 to 10% by weight, in particular from 0.5 to 5% by weight based on the formulation as a whole.

Likewise effective for purposes of the invention are hair treatment agents which contain as further components amino group-containing silicone oils, for example the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 949 emulsion (containing a hydroxylamino-containing silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquatery polydimethyl siloxanes, Quaternium-80).

Particularly preferred are hydroxylamino-containing silicones.

The compositions according to the invention contain the amino group-containing silicone oils in quantities of from 0.1 to 10% by weight, preferably in quantities of from 0.5 to 5% by weight.

One preferred embodiment consists of hair treatment agents for colouring and tinting hair which contain the active substance complexes according to the invention.

These agents contain what are known as "direct" dyes and/or precursors of oxidation dyes.

Direct dyes are usually nitrophenylenediamines, nitroaminophenols, azo dyes, anthrachinones or indophenols. Preferred direct dyes are the compounds known under the international names or trade names HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet I, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17, as well as 4-amino-2-nitrodiphenylamine-2-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, hydroxyethyl-2-nitro-toluidine, picramic acid, 2-amino-6-chloro-4-nitrophenol 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

Direct dyes according to the invention are also understood to include natural dyes such as those found in, for example, Henna red, Henna neutral, Henna black, chamomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet root.

The compositions according to the invention according to this embodiment contain the direct dyes preferably in a quantity of from 0.01 to 20% by weight, based on the colorant as a whole.

Other dye components contained in the colorants according to the invention may also be indoles and indolines, as well as their physiologically compatible salts. Preferred examples are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole. Also preferred are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline,

N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid, 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline.

Hair colorants contain as precursors of oxidation dyes what are known as developer and coupler components. The developer components form the actual dyes with one another under the influence of oxidizing agents or atmospheric oxygen or by coupling with one or more coupler components.

The developer components used are usually primary aromatic amines containing another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof.

Preferred developer components according to the invention are p-phenylenediamine, p-toluylenediamine, p-aminophenol, o-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)ethanol, 1-phenyl-3-carboxyamido-4-amino-pyrazolone-5, 4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2-hydroxymethylamino-4-aminophenol, 4,4'-diaminodiphenylamine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, bis(2-hydroxy-5-aminophenyl)methane, 1,4-bis(4-aminophenyl)diazacycloheptane, 1,3-bis(N(2-hydroxyethyl)-N(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)phenol, as well as 4,5-diaminopyrazole derivatives according to EP 0 740 741 or WO 94/08970 such as, for example, 4,5-diamino-1-(2'-hydroxyethyl)pyrazole.

Particularly preferred developer components are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine and 4-hydroxy-2,5,6-triaminopyrimidine.

As coupler components, m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives are normally used.

Preferred coupler components according to the invention are 1-naphthol, pyrogallol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, o-aminophenol, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 1-phenyl-3-methyl-pyrazolone-5, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)propane, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, 2,6-dihydroxypyridine, 2,6-diaminopyridine, 2-amino-3-hydroxypyridine, 2,6-dihydroxy-3,4-diaminopyridine, 3-amino-2-methylamino-6-methoxypyridine, 4-amino-2-hydroxytoluene, 2,6-bis-(2-hydroxyethylamino)toluene, 2,4-diaminophenoxyethanol, 1-methoxy-2-amino-4-(2-hydroxyethyl amino)benzene, 2-methyl-4-chloro-5-aminophenol, 6-methyl-1,2,3,4-tetrahydroquinoxaline, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, 2,6-dimethyl-3-aminophenol, 3-amino-6-methoxy-2-methylaminophenol, 2-hydroxy-4-aminophenoxyethanol, 2-methyl-5-(2-hydroxyethylamino)phenol and 2,6-dihydroxy-3,4-dimethylpyridine.

Particularly preferred coupler components are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol and 2,6-dihydroxy-3,4-diaminopyridine.

The hair colorants according to the invention contain both the developer components and the coupler components preferably in a quantity of from 0.005 to 20% by weight, based in each instance on the colorant without the oxidizing agent preparation. Here, developer components and coupler components are generally used in approximately molar quantities relative to one another. Even if the molar use has proved to be effective, a certain excess of individual oxidation dye precursors is not disadvantageous, so that developer components and coupler components can be contained in a molar ratio of from 1:0.5 to 1:2.

In principle, the colour may be oxidatively developed with atmospheric oxygen. However, a chemical oxidizing agent is preferably used, particularly when a brightening effect upon human hair is desired in addition to the colouring. Suitable oxidizing agents are persulfates, chlorites and particularly hydrogen peroxide or addition products thereof with urea, melamine and sodium borate. It is also possible to carry out oxidation with enzymes. Here, the enzymes may serve to transfer atmospheric oxygen to the developer components or to enhance the effect of oxidizing agents present in smaller quantities. One example of an enzymatic process is the procedure whereby the effect of small quantities (for example 1% and less, based on the formulation as a whole) of hydrogen peroxide is enhanced by peroxidases.

Colorations of particular colour depth can be achieved if the hair treatment agents also contain, in addition to the dyes and/or dye precursors, an oil of the meadowfoam plant (INCI name: Meadowfoam Seed Oil).

Another preferred embodiment consists of agents for the lasting deformation of human hair which contain as care components the combination of active substances according to the invention.

A lasting hair deformation is, according to the known permanent wave method, carried out in such a way that the hair is mechanically deformed and the deformation fixed, for example by putting the hair in curlers or rollers. Before and/or after this deformation, the hair is treated with the aqueous preparation of a keratin-reducing substance and, after a contact time, rinsed with water or an aqueous solution. In a second step, the hair is then treated with the aqueous preparation of an oxidizing agent. After a contact time, this is also rinsed out of the hair and the hair freed from the mechanical deformation aids (curlers, rollers).

The aqueous preparation of the keratin-reducing agent is usually alkalized so that the hair swells and the keratin-reducing substance is in this way enabled to penetrate deeply into the hair. The keratin-reducing substance splits a portion of the disulfide bonds of the keratin to -SH groups, so that the peptide linkage is loosened and, as a result of the stretching of the hair by its mechanical deformation, the keratin structure is reoriented. Under the influence of the oxidizing agent, disulfide bonds are re-established and, in this way, the keratin structure is re-fixed in the given deformation.

According to the invention, the reaction products of the components (A) and (B) can be added both to the keratin-reducing agent (waving agent) and to the keratin-oxidizing agent (fixing solution) for permanent wave treatment.

Particularly preferred is the use of the agents according to the invention in fixing solutions.

The reducing agents used nowadays are almost exclusively alkalized (pH values of from 8.5 to 9.5) solutions of thioglycolic acid or the salts or esters thereof, as well as thiolactic acid, cysteamine, thiomalic acid or α -mercaptoethanesulfonic acid.

Oxidizing agents, for example sodium bromate, potassium bromate, hydrogen peroxide and the stabilizers normally used to stabilize aqueous hydrogen peroxide preparations, are a compulsory component of the fixing agents. The pH value of such aqueous H_2O_2 preparations, which normally contain about 0.5 to 3.0% by weight H_2O_2 , is preferably in the range from 2 to 4; it is adjusted by anorganic acids, preferably phosphoric acid. Bromate-based fixing agents contain the bromates usually in concentrations of from 1 to 10% by weight, and the pH value of the solutions is adjusted to from 4 to 7. Likewise suitable are enzyme-based fixing agents (peroxidases) which contain no or only small quantities of oxidizing agents, particularly H_2O_2 .

The aqueous hair treatment agent, depending on the type of application thereof, may also contain, in the usual quantities known to the specialist:

- anionic surfactants such as, for example, alkylbenzenesulfonates, glycerol ether sulfonates, alkanesulfonates, alkyl sulfates, alkyl ether sulfates with a conventional or a narrowed homolog distribution, glycerol ether sulfates, monoglyceride (ether) sulfates, hydroxy mixed ether sulfates, alkyl oligoglucoside sulfates, isethionates, taurides, sarcosinates, alkyl ether carboxylic acid salts, sulfosuccinates, sulfotriglycerides and alkyl (ether) phosphates.
- cationic surfactants such as, for example, quaternary ammonium compounds, amidoamines and quaternized esters and protein hydrolysates,
- zwitterionic surfactants such as, for example, betaines,
- ampholytic surfactants,
- nonionic polymers such as, for example, polyvinylpyrrolidone, vinylpyrrolidone/vinylacetate copolymers and cellulose ethers,
- structurants such as glucose and maleic acid,
- hair conditioning compounds such as phospholipids, for example soy lecithin, egg lecithin and kephalins, as well as silicone oils,
- protein hydrolysates, particularly elastin, collagen, keratin, milk protein, soy protein and wheat protein hydrolysates, condensation products thereof with fatty acids, and quaternized protein hydrolysates,
- perfume oils and dimethyl isosorbide,
- solubility promoters such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- dyes,
- anti-dandruff agents such as piroctone olamine and zinc omadine,
- other substances for adjusting the pH value,
- active substances such as panthenol, allantoin, pyrrolidone carboxylic acid and salts thereof, plant extracts and vitamins,
- sun protection factors,
- consistency factors such as sugar esters, polyol esters or polyol alkyl ethers,
- waxes, such as beeswax and montan wax,
- fatty acid alkanolamides,
- complexing agents such as EDTA, NTA and phosphonic acids,
- swelling and penetration agents such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates,

- opacifiers, such as Latex,
- pearlizers, such as ethylene glycol mono- and distearate,
- propellants, such as propane/butane mixtures, N₂O, dimethyl ether, CO₂ and air, and
- antioxidants,
- reducing agents such as, for example, thioglycolic acids and derivatives thereof, thiolactic acid, cysteamine, thiomalic acid and α -mercaptoethanesulfonic acid,
- oxidizing agents, such as hydrogen peroxide, potassium bromate and sodium bromate.

If very especially effective treatment agents are desired for hair care, the known cationic hair care polymers, such as, for example, the products marketed under the trade names Polymer® JR, Cosmedia Guar®, Luviquat®, Mirapol® A15, Gafquat®, Merquat®, Hercules® PD170, Cartaretine® F4, Polyquart® H and Polymin® HS can, of course, be used in addition to the care mixture described. The cationic polymers may be contained in quantities of from 1 to 10% by weight, based on the hair treatment agent.

The care properties of the hair treatment agents according to the invention are particularly effective if they are formulated for shampoos, restorers, rinses and direct dye-containing hair colour changing agents in such a way that they have a pH value of from 4 to 8. Hair treatment agents which contain precursors of oxidation dyes optimally develop their care effect if these precursors have a pH value in the range of from 6 to 11, more particularly from 8 to 10.

The present application also relates, finally, to the use of the aforementioned agents for treating skin and hair.

The following examples are intended to explain more precisely the object of the patent.

Embodiment examples

1. Preparation of the hair treatment agents

All quantities in the formulations are weight fractions

	Formulation 1	Formulation 2	Formulation 3	Formulation 4	Formulation 5
Dilauroyl ethylenediamine diacetic acid (100% active substance)	1.0	2.0	1.0	2.0	—
Hydrenol® D ¹	—	—	5.0	5.0	5.0
Texapon NSO ²	—	—	—	—	8.0
NaOH	ad pH 8.5	ad pH 8.5	ad pH 8.5	ad pH 8.5	ad pH 8.5
Water	ad 100.0	ad 100.0	ad 100.0	ad 100.0	ad 100.0

¹ C₁₆-C₁₈-fatty alcohol (INCI name: cetearyl alcohol) (HENKEL)

² Lauryl ether sulfate, sodium salt (28% active substance; INCI name: sodium laureth sulfate) (HENKEL)

2. Examination of the effectiveness of the formulations

a) Intentional damage to strands of hair

Dry hair strands weighing approximately 2 g (Fischbach and Miller type 6923) were bleached once with 8 g of a bleaching mixture (market product Poly Blond Medium brightener) for a half hour. After the bleaching mixture was washed out, the hair strands were immediately, without intermediate drying, subjected to a permanent wave treatment with the market product Poly Lock Normal. The exposure time for waving components and fixing components was 30 and 15 minutes respectively. After the fixing components were rinsed out, the strands were dried and conditioned for at least two days under ambient conditions.

b) Test of wet combability

Before the test, each rinsed hair strand was thoroughly shampooed with 0.2 ml of a 50% aqueous solution of Texapon® NSO and then rinsed off. 0.5 ml of the formulation to be tested was then massaged evenly into the hair, left in the hair for one minute and then carefully rinsed out. Combing was then performed with a fine-tined comb made of hard rubber, and the combing resistance was rated subjectively. The rating was given according to a rating scale of from 1 (= very good) to 5 (= very poor). Subsequently, the strand was thoroughly shampooed with 0.2 ml of a 50% aqueous solution of Texapon® NSO and thoroughly rinsed off. The wet combability of the strands treated in this way received a rating of 5.

c) Assessment of the formulations

Formulation No.	Rating
1	4
2	3-4
3	1-2
4	1
5	4
50% Texapon® solution	5

As may be seen from the table, a synergistic improvement of wet combability occurs when a combination of effective care substances according to the invention is used (Examples 3 and 4).

3. Other formulation examples

a) Rinsable skin care emulsions

An oil-in-water skin emulsion B1 according to the invention and a skin care emulsion V1 serving as a comparison were prepared.

Raw material	Formulation B1	Formulation V1
Dilauroyl ethylenediamine diacetic acid (100% aktive substance)	4.0	—
Eumulgin® B2 ³	—	2.0
Akypo® Soft RLM 100 NV ⁴	—	10.0
Stenol® 1618 ⁵	3.0	3.0
Paraffin oil, perliquidum	2.0	2.0
Cetiol SN ⁶	1.0	1.0
Triethanolamine	ad pH 8.2	ad pH 8.2
Perfume oil	0.3	0.3
Water	ad 100.0	ad 100.0

³ Cetyl stearyl alcohol with 20 EO units (INCI name: cetareth-20)
(HENKEL)

⁴ Lauryl alcohol with approx. 10 EO units, acetic acid sodium salt (INCI name: sodium laureth-11 carboxylate, approx. 22% active substance) (KAO)

⁵ C₁₆- to C₁₈-fatty alcohol (INCI name: cetearyl alcohol) (HENKEL)

⁶ Isononanoic acid C₁₆- to C₁₈-alkyl ester (INCI name: cetearyl isononanoate)
(HENKEL)

The emulsions were applied to the wet skin after the skin was washed. After it was rinsed off, the skin treated with the formulation B1 according to the invention felt distinctly smoother and softer to the touch.

b) Hair tinting, blond

Raw material	Formulation B2	Formulation V2
Dilauroyl ethylenediamine diacetic acid (100% active substance)	2.0	2.0
Starch, soluble	1.0	1.0
Stenol® 1618	3.0	—
Cutina MD ⁷	1.0	—
Natrosol®HR250 ⁸	1.0	1.0
HC Blue 2	0.05	0.05

HC Yellow 2	0.06	0.06
Arianor Sienna brown	0.04	0.04
2-amino-6-chloro-4-nitrophenol	0.015	0.015
1,4-bis(2'-hydroxyethyl)amino-2-nitrobenzene	0.06	0.06
Monoethanolamine	ad pH 8.2	ad pH 8.2
Water	ad 100.0	ad 100.0

7 Mono- and diglycerides of palmitic and stearic acid (INCI name: glyceryl stearate) (HENKEL)

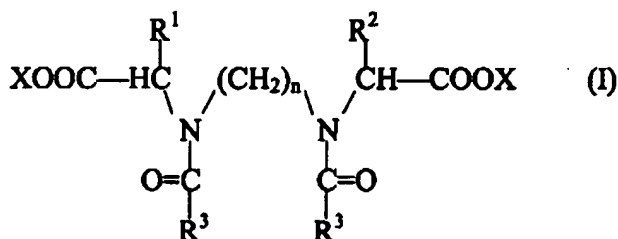
8 Hydroxyethylcellulose (INCI name: hydroxyethylcellulose) (HERCULES)

Intentionally damaged hair strands were coloured (see 2a) with 2 g of colouring cream per strand. After an exposure time of 20 minutes, the strands were thoroughly rinsed with water. The wet combability of the strands which were treated with the formulation B2 according to the invention received a rating of 2, the wet combability of the comparison strand (Formulation V2) a rating of 4.

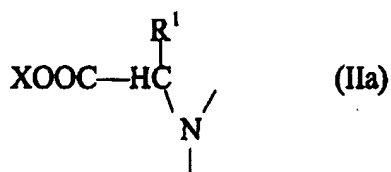
Claims

1. Treatment agents for skin and hair care, comprising as active care substances a mixture of

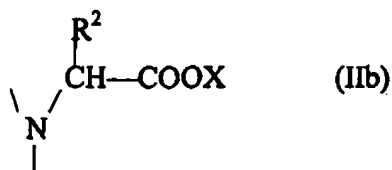
(A) at least one diacyl-alkenyldiaminodicarboxylic acid according to formula (I)



where the units



and



stand in each instance, independently of one another, for an α -aminocarboxylic acid, R^3 stands for a saturated, mono- or polyunsaturated, branched or unbranched C_1 - to C_{21} -alkyl radical, n stands for an integer from 1 to 20 and X stands for hydrogen or for an equivalent of an alkali, alkaline earth, ammonium, alkylammonium, hydroxyalkylammonium and/or glucammonium cation, and

(B) at least one oil, fat and/or wax.

2. Treatment agents for skin and hair care according to claim 1, wherein the component (A) is a compound of formula (I), wherein R^1 and R^2 stand for hydrogen.
3. Treatment agents for skin and hair care according to one of the claims 1 or 2, wherein the component (A) is a compound of formula (I) and R^3 stands for a C_8 - to C_{18} -alkyl radical, particularly for a C_{12} -alkyl radical.
4. Treatment agents for skin and hair care according to one of the claims 1 to 3, the component (B) can be a C_6 - to C_{22} -fatty alcohol or a C_6 - to C_{22} -fatty acid.
5. Treatment agents for skin and hair care according to one of the claims 1 to 4, comprising as a further component at least one nonionic surfactant, particularly an alkyl polyglycoside.
6. Treatment agents for skin and hair care according to one of the claims 1 to 5, further comprising as an additional hair fixing component water-soluble starch and/or at least one acyl lactylate.
7. Treatment agents for skin and hair care according to one of the claims 1 to 6, further comprising as an additional care component an amino group-containing silicone oil.
8. Treatment agents for skin and hair care according to one of the claims 1 to 7, further comprising direct dyes and/or precursors of oxidation dyes.
9. Treatment agents for skin and hair care according to one of the claims 1 to 8, wherein said agents serve to lastingly deform human hair.
10. Use of one of the agents of claims 1 to 5 for skin treatment.
11. Use of one of the agents of claims 1 to 9 for hair treatment.

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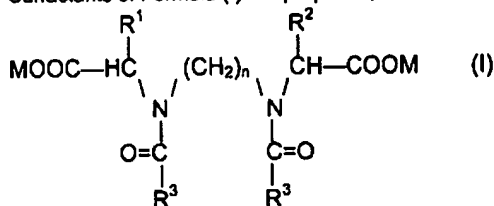
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(56) Publications considered in assessing patentability:
WO 95 19 955 A1

(54) Gemini surfactants

(57) Surfactants of Formula (I) are proposed,



where R¹ and R² stand for an amino carboxyl acid radical, R³ stands for an alkyl radical having from 1 to 21 carbon atoms and M stands for an alkali metal. The substances are suitable for the preparation of a large number of surface-active agents.

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DESCRIPTION

Introduction

The invention relates to new gemini surfactants, a method for the preparation thereof, and their use in the preparation of surface-active agents, especially in combination with other surfactants.

Prior art

In the area of surfactants there is an ever-present need for more powerful and, at the same time, especially skin-compatible new substances that have synergistic effects when used with other surfactants.

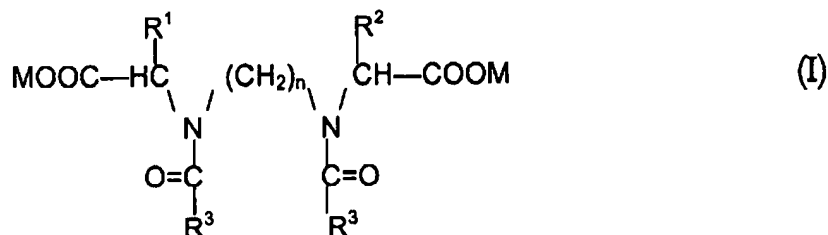
At the end of the 1980s the term "gemini surfactants" was coined for a class of surfactants in which two amphiphiles (surfactants) are linked to one another through a bonding link, the so-called "spacer." "Gemini surfactants" possess interesting surfactant properties and a high potential for synergistic interactions with conventional surfactants (Li D. Song, M. J. Posen, *Chemtech* (1993), pp. 30—33; F. Menger, C. A. Littau, *J. Am. Chem. Soc.* 115 (1993), pp. 100083-90; Y. Zhu, A. Masuyama, M. Okahara, *J. Am. Oil Chem. Soc.*, Vol. 67 (1990), pp. 459—463). "Gemini surfactants" have already attracted widespread interest. There have now been a number of patent applications in this field of work (DE 43 21 022, WO 95/19951, WO 95/19953-55, WO 95/20026 (Procter & Gamble), JP 071799 (Kao Corp.), EP 0697244 and EP 0697245 (Rhône-Poulenc)). The preparation of multifunctional compounds does not always prove to be easy and often fails to deliver the desired products. Because of the large number of functional groups, undesired side reactions can occur, or the product may itself further react with the functional groups.

Apart from the "gemini surfactants," N-acylamino acids, for example N-acyl glutamate or N-acyl aspartate, have gained importance in recent years as especially mild surfactants that can be used in cosmetic applications (A. Turowski, W. Skrypzak, A. Reng, P. Jürges, *Parfümerie und Kosmetik*, 76 (1995), pp. 16—27).

The complex aim of the present invention is to provide new compounds that combine the advantages of the "gemini surfactants" with especially good skin-compatibility and that can be synthesized easily.

DESCRIPTION OF THE INVENTION

The invention accordingly relates to compounds of the formula (I)

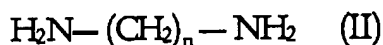


wherein R¹ and R² stand for the radical of an aminocarboxylic acid, R³ for an alkyl radical having from 1 to 21 carbon atoms, and M for an alkali metal, alkaline earth metal, ammonium, alkylammonium, hydroxalkylammonium, and/or glucammonium, and wherein n may assume values from 1 to 20; and also a method for their preparation and their use especially as surfactants. Surprisingly, it was found that substances according to the formula (I) have good surfactant

properties and are at the same time very mild. In addition, the invention is based on a method whereby the substances according to the invention can be easily prepared. The substances according to the invention, especially when used in combination with other surfactants, demonstrate very good application properties, such as a reduction in surface tension and interfacial wetting.

In one embodiment, to prepare the compounds according to claim 1 with $n = 1$, preferably a condensation of aminocarboxylic acids with formaldehyde is carried out according to a method known from the literature (E. Skrzydlewska, *Pol. J. Environ. Stud.* 3 (1994), pp. 13–20) and subsequently acylated in the usual way, for example according to the Schotten-Baumann method with an acid chloride. Alternatively, a coupling of already acylated amino acids with formaldehyde can also occur (N. Noulet, D. Tome, *J. Chim. Phys. Phys.-Chim. Biol.* 81 (1984), pp. 173-177.).

To prepare compounds with n greater than/equal to 1, the corresponding diamines according to formula (II)



with n greater than/equal to 1, can be reacted with formaldehyde, HCN (R. P. Lastovskii, et al, *Otkryticya, Izobret, Prom. Obratsy, Tovornye Znaki*, 47 (1970), p. 28) or chloracetic acid (FR 1554236) according to the usual methods of preparative organic chemistry and subsequently acetylated in the likewise known way. According to the present invention, compounds of formula (II) are preferably used in which $n = 1$ to 12.

An especially preferred embodiment, in which compounds are obtained for which $n=2$, consists in the reaction of commercially available N,N'-ethylenediaminediacetate, which is acylated with acid chloride according to the known method (Schotten Baumann method).

The acylation is usually carried out at a pH value in the range from 9 to 10. The carboxylic acid derivative is used as an acylating agent usually in a two- to five-fold, preferably in a three-fold molar excess, based on the diamine to be acylated.

Subsequent to the reaction, the reaction medium is adjusted with a mineral acid, preferably HCl, to a pH value of from 1 to 4, preferably to a value of from 2 to 3. In order to subsequently obtain the corresponding salt according to formula (I), the reaction product is neutralized with a base. The base is preferably the same base that was already used in connection with the acylation.

Aminocarboxylic acids

Aminocarboxylic acids are to be understood as meaning in principle all carboxylic acids, preferably those having from 1 to 20 carbon atoms, with one or more amino groups in the molecule. In a narrower sense they are, in the context of the present invention, the 20 naturally occurring L- α -aminocarboxylic acids participating in the synthesis of proteins, for example L-aspartate, L-glutamate, L-lysine, L-arginine, L-histidine, L-citrulline, L-homocysteine, L-homoserine, hydroxyproline, hydroxylysine, L-ornithine, sarcosine, L-alanine, L-valine, L-leucine, L-isoleucine, L-proline, L-tryptophan, L-phenylalanine, L-methionine, L-serine, L-tyrosine, L-threonine, L-cysteine, L-asparagine, L-glutamine and preferably glycine. Apart from the naturally occurring L- α -aminocarboxylic acids, the corresponding D-amino acids or other synthetic aminocarboxylic acids, especially α -aminocarboxylic acids according to formula (III), can also be used,



where R^4 is H, an alkyl radical or aryl radical having in each instance from 1 to 20 carbon atoms and which can carry heteroatoms such as N, O, S also in the form of further functional groups. R^4

corresponds to R^1 and R^2 in formula (I) after the method is carried out.

Carboxylic acid derivatives

Acylation at nitrogen can be carried out according to all the usual methods known from the literature, in particular with carboxylic acid derivatives, preferably fatty acid derivatives, for example fatty acid halogenides, in particular fatty acid chlorides. In addition, other carboxylic acid derivatives are also suitable, for example esters or even anhydrides, which can also be anhydrides of a carboxylic acid with sulfur trioxide or carbon dioxide. The carboxylic acid derivatives that are particularly suitable according to the invention contain from 2 to 22, preferably from 6 to 22, carbon atoms. Typical examples are caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid, and also technical-grade mixtures thereof, which are formed for example in the pressure cracking of natural fats and oils, in the reduction of aldehydes from the Roelen oxo synthesis or the dimerisation of unsaturated fatty acids.

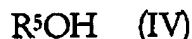
Preference is given to technical fatty acids having from 12 to 18 carbon atoms, for example coconut, palm, palm kernel or tallow fatty acid.

Bases

Alkali metal, alkaline earth metal, ammonium, alkylammonium, hydroxyalkylammonium, and/or glucammonium hydroxides can usually be used as a base. In addition, organic amines, for example chinoline, pyridine and/or guanidine, are also suitable. Particular preference is given to using sodium, potassium and ammonium hydroxide. Combinations of different bases are also possible. For example, in combination with ammonium hydroxide other, less odour-intensive amines, for example triethanolamine, can also be added in smaller quantities to obtain a product with an improved odour.

Organic solvents

The acylation can be carried out in aqueous solution; preferably, however, organic solvents are added for improved solubility. In principle, all water-miscible organic solvents are suitable, especially alcohols of the formula (IV)



where R^5 stands for an alkyl radical having from 1 to 8, preferably from 2 to 4, carbon atoms, or for acetone. The amount of organic solvents can be up to 80% by volume of the total solvent, in particular from 20 to 50% by volume. Preference is given to the use of acetone, and particular preference is given to the use of isopropanol.

In a further method, it is also possible to work without water with purely organic solvents, for example ethers or ketones, if a salt that is soluble or at least partially soluble in the corresponding solvents is used with, for example, chinoline, pyridine or guanidine, or even an ester of the amino acid. If an ester of the amino acid is used, then a selective hydrolysis of the ester bond is required after the acylation.

Surfactants

The compounds according to the invention can be used as surfactants in the usual formulations. They combine well with all known surfactants, which can be anionic, cationic, nonionic, amphoteric or zwitterionic surfactants.

Typical examples of anionic surfactants are alkylbenzenesulfonates, alkanesulfonates, olefinsulfonates, alkyl ether sulfonates, glycerol ether sulfonates, α -methyl ester sulfonates, sulfo fatty acids, primary and secondary alkyl sulfates, fatty alcohol ether sulfates, glycerol ether sulfates, hydroxy-mixed ether sulfates, monoglyceride (ether) sulfates, fatty acid amide (ether) sulfates, mono- and dialkyl sulfosuccinates, mono- and dialkyl sulfosuccinamates, sulfotriglycerides, amide soaps, ether carboxylic acids and salts thereof, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, acyl lactylates, acyl tartrates, acyl glutamates, acyl aspartates, α -hydroxycarboxylic acid ester sulfates, alkyl oligoglucoside sulfates, protein fatty acid condensates (especially plant products based on wheat) and alkyl (ether) phosphates. Where the anionic surfactants contain polyglycol ether chains, these chains may have a conventional, though preferably a narrowed, homolog distribution.

Typical examples of nonionic surfactants are fatty alcohol polyglycol ethers, alkylphenol polyglycol ethers, fatty acid polyglycol esters, fatty acid amide polyglycol ethers, fatty amine polyglycol ethers, alkoxyated triglycerides, mixed ethers or mixed formals, alk(en)yl oligoglycosides, fatty acid N-alkylglucamides, protein hydrolysates (in particular plant products based on wheat), polyol fatty acid esters, sugar esters, sorbitan esters, polysorbates, and amine oxides. Where the nonionic surfactants contain polyglycol ether chains, these chains may have a conventional, though preferably a narrowed, homolog distribution.

Typical examples of cationic surfactants are quaternary alkylammonium compounds and ester quats, in particular quaternized fatty acid trialkanolamine ester salts.

Typical examples of amphoteric or zwitterionic surfactants are alkyl betaines, alkylamido betaines, aminopropionates, aminoglycinates, imidazolinium betaines, and sulfobetaines.

The surfactants mentioned are without exception known compounds. With regard to the structure and preparation of these substances, reference may be made to the relevant overview works, for examples J. Falbe (ed.), "Surfactants in Consumer Products", Springer Verlag, Berlin, 1987, pp. 54—124, or J. Falbe (ed.), "Katalysatoren, Tenside und Mineralöladditive", Thieme Verlag, Stuttgart, 1978, pp. 123—217.

Preference is given to using the substances according to the invention in combination with alkyl oligoglucosides, fatty acid N-alkylglucamides, fatty alcohol ether sulfates, fatty alcohol sulfates, monoglyceride sulfates and fatty alcohol polyethylene glycol ethers.

Commercial applicability

The detergent mixtures according to the invention synergistically strengthen cleaning and foaming ability. A further object of the invention therefore relates to its use in the preparation of surface-active agents, namely:

- Pulverulent multi-purpose detergents comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Liquid multi-purpose detergents comprising from 10% to 70% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Liquid mild detergents comprising from 10% to 50% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Brightening agents comprising from 10% to 50% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Hand dishwashing detergents comprising from 10% to 50% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.

- Rinse aids comprising from 10% to 50% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Liquid cleaners and disinfectants comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Bar soaps of the combi-bar type, comprising from 1% to 2% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Syndet soaps comprising from 1% to 2% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Hair shampoos comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Hair conditioners comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Hair dyes comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Hair waving agents comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Foam baths comprising from 10% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Textile and fibre auxiliaries comprising from 1% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Leather greasing agents comprising from 1% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Flotation aids comprising from 1% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.
- Aids for drying solids material, comprising from 1% to 30% by weight — based on the composition — of the detergent mixtures according to the invention, and also customary auxiliaries and additives.

They are also suitable for the preparation of cosmetic and/or pharmaceutical formulations, in particular creams, ointments and lotions. Particular preference is given to the use of detergent mixtures according to the invention for the preparation of manual dishwashing detergents, hair shampoos and skin care products.

Surfactants

The compositions mentioned above may comprise, as auxiliaries and additives, primarily further anionic, nonionic, cationic, amphoteric and/or zwitterionic surfactants, which are the surfactants already mentioned.

Further auxiliaries and additives

The formulations according to the invention, for example hair shampoos, hair lotions, foam baths, creams, lotions or ointments, can also contain, as further auxiliaries or additives, builders, salts, bleaches, bleach activators, optical brighteners, graying inhibitors, solubility promoters, enzymes, oil bodies, emulsifiers, superfatting agents, stabilizers, waxes, consistency regulators, thickeners, cation

polymers, silicon compounds, biogenic agents, film formers, preservatives, dyes and fragrances.

Customary builders are sodium aluminium silicates (zeolites), phosphates, phosphonates, ethylenediaminetetraacetic acid, nitrilotriacetate, citric acid and/or polycarboxylates. Suitable salts or standardizing agents are, for example, sodium sulfate, sodium carbonate or sodium silicate (water glass). As typical isolated examples of other additives, mention may be made of sodium borate, starches, sucrose, polydextrose, TAED, stilbene compounds, methylcellulose, toluenesulfonate, cumenesulfonate, long-chain soaps, silicones, mixed ethers, lipases and proteases.

As stabilizers, metal salts of fatty acids, for example magnesium, aluminium and/or zinc stearate, can be used.

Suitable oil bodies are, for example, Guerbet alcohols based on fatty alcohols having from 6 to 18, preferably from 8 to 10, carbon atoms, esters of linear C_6-C_{20} fatty acids with linear C_6-C_{20} fatty alcohols, esters of branched C_6-C_{13} carboxylic acids with linear C_6-C_{20} fatty alcohols, esters of linear C_6-C_{18} fatty acids with branched alcohols, particularly 2-ethylhexanol, esters of linear and/or branched fatty acids with polyhydric alcohols (for example dimerdiol or trimetriol) and/or Guerbet alcohols, triglycerides based on C_6-C_{10} fatty acids, plant oils, branched primary alcohols, substituted cyclohexanes, Guerbet carbonates, dialkyl ethers and/or aliphatic or naphthenic hydrocarbons.

As emulsifiers or co-emulsifiers, nonionogenic, ampholytic and/or zwitterionic surfactant compounds can be used that are distinguished by a lipophilic, preferably linear alkyl or alkenyl group and at least one hydrophilic group. This hydrophilic group can be either an ionogenic or nonionogenic group. Nonionogenic emulsifiers comprise as a hydrophilic group, for example, a polyol group, a polyalkylene glycol ether group or a combination of a polyol and polyglycol ether group.

Preference is given to those compositions that comprise, as o/w emulsifiers, nonionogenic surfactants from at least one of the following groups:

- (a1) Addition products of from 2 to 30 mol of ethylene oxide and/or from 0 to 5 mol of propylene oxide with linear fatty alcohols having from 8 to 22 carbon atoms, with fatty acids having from 12 to 22 carbon atoms and with alkyl phenols having from 8 to 15 carbon atoms in the alkyl group;
- (a2) C_{12-18} fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide with glycerol;
- (a3) Glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids having from 6 to 22 carbon atoms and ethylene oxide addition products thereof;
- (a4) Alkyl mono- and oligoglycosides having from 8 to 22 carbon atoms in the alkyl radical and ethoxylated analogs thereof;
- (a5) Addition products of from 15 to 60 mol of ethylene oxide with castor oil and/or hydrogenated castor oil;
- (a6) Polyol esters and especially polyglycerol esters, for example polyglycerol polyricinoleate or polyglycerol poly-12-hydroxystearate. Likewise suitable are mixtures of compounds from several of these substance classes.

The addition products of ethylene oxide and/or of propylene oxide with fatty alcohols, fatty acids, alkylphenols, glycerol mono- and diesters and also sorbitan mono- and diesters of fatty acids, or with castor oil, are known, commercially available products. They are homolog mixtures, the average degree of alkoxylation of which corresponds to the ratio of the amounts of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C_{12-18} fatty acid mono- and diesters of addition products of ethylene oxide with glycerol are known from DE-PS 20 24 051 as fat-restoring substances for cosmetic preparations.

C_{8-18} alkyl mono- and oligoglycosides, their preparation and their use as surface-active substances are known for example from US 3,839,318, US 3,707,535, US 3,547,828, DE-OS 19 43 689, DE-OS

20 36 472 and DE-A1 30 01 064, as well as EP-A 0 077 167. They are prepared especially by reacting glucose or oligosaccharides with primary alcohols having from 8 to 18 carbon atoms. Suitable glycoside radicals include monoglycosides in which a cyclic sugar radical is glycosidically bonded to the fatty alcohol and also oligomeric glycosides having a degree of oligomerization of up to preferably about 8. The degree of oligomerization is a statistical average value based on a homolog distribution customary for such technical-grade products.

It is also possible to use zwitterionic surfactants as emulsifiers. The term "zwitterionic surfactants" denotes surface-active compounds that carry at least one quaternary ammonium group and at least one carboxylate and a sulfonate group in the molecule. Zwitterionic surfactants that are especially suitable are the so-called betaines, such as N-alkyl-N,N-dimethylammonium glycinate, for example cocoalkyldimethylammonium glycinate, N-acylaminoethyl-N,N-dimethylammonium glycinate, for example cocoacylaminoethyl-N,N-dimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethylimidazolines each having from 8 to 18 carbon atoms in the alkyl or acyl group and also cocoacylaminoethylhydroxyethylcarboxymethylglycinate. Special preference is given to the fatty acid amide derivative known by the CTFA name cocamidopropyl betaine. Likewise suitable as emulsifiers are ampholytic surfactants. Ampholytic surfactants are to be understood as those surface-active compounds that contain in the molecule, in addition to a C_{8-18} alkyl or acyl group, at least one free amino group and at least one $-COOH$ or $-SO_3H$ group, and that are capable of forming internal salts. Examples of suitable ampholytic surfactants are N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids, each having approximately from 8 to 18 carbon atoms in the alkyl group. Ampholytic surfactants to which special preference is given are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C_{12-18} acylsarcosine.

As w/o emulsifiers there come into consideration:

- (b1) addition products of from 2 to 15 mol of ethylene oxide with castor oil and/or hydrogenated castor oil;
- (b2) partial esters based on linear, branched, unsaturated or saturated C_{12-22} fatty acids, ricinoleic acid and also 12-hydroxystearic acid and on glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (e.g. sorbitol) and also polyglucosides (e. g. cellulose);
- (b3) trialkyl phosphates;
- (b4) wool wax alcohols;
- (b5) polysiloxane/polyalkyl/polyether copolymers and corresponding derivatives;
- (b6) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol in accordance with DE-PS 11 65 574; and also
- (b7) polyalkylene glycols.

Superfating agents that can be used are substances such as, for example, polyethoxylated lanolin derivatives, lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, where the latter also serve as foam stabilizers. As consistency regulators there come into consideration primarily fatty alcohols having from 12 to 22 carbon atoms and preferably from 16 to 18 carbon atoms. Preference is given to a combination of these substances with alkyl oligoglucosides and/or fatty acid N-methylglucamides of identical chain length and/or polyglycerol poly-12-hydroxystearates. Suitable thickeners include, for example, polysaccharides, especially xanthan gum, guar-guar, agar-agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, also relatively high molecular weight polyethylene glycol mono- and diesters of fatty acids, polyacrylates, polyvinyl alcohol and polyvinylpyrrolidone, surfactants such as, for example, fatty alcohol ethoxylates with restricted homolog distribution or alkyl oligoglucosides as well as electrolytes such as sodium chloride and ammonium chloride.

Suitable cationic polymers are, for example, cationic cellulose derivatives, cationic starch, copolymers of diallylammonium salts and acrylamides, quaternized vinylpyrrolidone/vinyl imidazole polymers, for example Luviquate®, condensation products of polyglycols and amines, quaternized collagen polypeptides, for example lauryldimonium hydroxypropyl hydrolyzed collagen (Lamequat® L), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers, for example amidomethicones, copolymers of adipic acid and dimethylaminohydroxypropyldiethylenetriamine (Cartaretin®), polyaminopolyamides as described, for example, in FR-A 22 52 840, and the crosslinked water-soluble polymers thereof, cationic chitin derivatives, for example of quaternized chitosan, optionally distributed as microcrystals, cationic guar gum, for example Jaguar® CBS, Jaguar® C-17, Jaguar® C-16, quaternized ammonium salt polymers, for example Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1.

Suitable silicone compounds are, for example, dimethyl polysiloxanes, methylphenyl polysiloxanes, cyclic silicones as well as amino, fatty acid, alcohol, polyether, epoxy, fluorine and/or alkyl modified silicon compounds. Superfatting agents that can be used are substances such as, for example, polyethoxylated lanolin derivatives, lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, where the latter also serve as foam stabilizers. Typical examples of fats are glycerides, while suitable waxes are inter alia beeswax, paraffin wax or microwaxes, optionally in combination with hydrophilic waxes, for example cetostearyl alcohol. As stabilizers, metal salts of fatty acids, for example magnesium, aluminium and/or zinc stearate, can be used. Biogenic active ingredients are understood as meaning, for example, plant extracts and vitamin complexes. Customary film formers include, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinylpyrrolidone, vinylpyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternized cellulose derivatives, collagen, hyaluronic acid or salts thereof, and similar compounds. Suitable preservatives are, for example, phenoxyethanol, formaldehyde solution, parabens, pentandiol or sorbic acid. Suitable pearling agents are, for example, glycol distearic acid esters such as ethylene glycol distearate, but also fatty acid monoglycol esters. Dyes that can be used are substances which are suitable and approved for cosmetic purposes, such as are listed, for example, in the publication "Kosmetische Färbemittel" [Cosmetic Colorants] from the Farbstoffkommission der Deutschen Forschungsgemeinschaft, Verlag Chemie, Weinheim, 1984, pp. 81—106. These dyes are usually used in concentrations of from 0.001 to 0.1% by weight, based on the overall mixture.

The total proportion of the auxiliaries and additives can be from 1 to 50, preferably from 5 to 40% by weight, based on the composition.

Examples

Preparation of ethylenediamine-N,N'-dilauroyl-N,N'-diacetic acid, Na salt

Example 1

35.2 g (0.2 mol) ethylenediamine-N,N'-diacetic acid was added to 300 ml of aqueous, alkaline NaOH solution having a pH value of from 9.5 to 10. 131.4 g (0.6 mol) of lauric acid chloride was added dropwise within one hour at 20°C as the pH value was continually adjusted with 50% by weight of NaOH. Subsequently stirring was continued for approximately one hour.

Further processing took place by acidification of the reaction mixture with HCl to pH = 2 and filtering off the acid reaction product. This was decocted twice with 150 ml petroleum ether and subsequently dried. If, in view of further use, a separation of the fatty acid resulting as an hydrolysis by-product is not required, then it can remain in the product.

The yield of acylation product based on the ethylenediamine-N,N'-diacetic acid was 53.8 g ethylenediamine-N,N'-dilauroyl-N,N'-diacetic acid (= 58%).

Example 2

The reaction was carried out as given in Example 1, but acetone was added to the aqueous solution, so that water/acetone in a ratio of 4:1 was present as a solvent.

The yield of acylation product based on the ethylenediamine-N,N'-diacetic acid was 82 g ethylenediamine-N,N'-dilauroyl-N,N'-diacetic acid (= 76%).

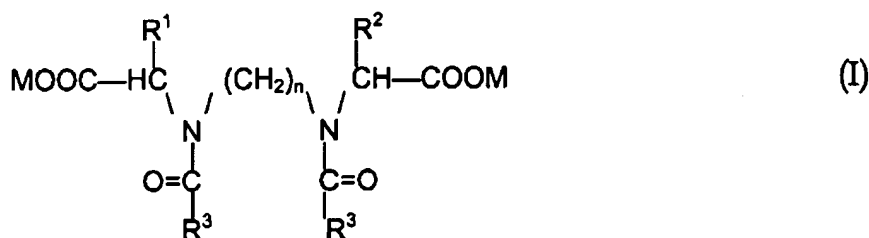
Example 3

The reaction was carried out as in Examples 1 and 2, but water/isopropanol in a ratio of 3:1 was used as a solvent. The yield of acylation product based on the ethylenediamine-N,N'-diacetic acid was 94.1 g = 87% ethylenediamine-N,N'-dilauroyl-N,N'-diacetic acid.

For the preparation of the sodium or potassium salt, the products obtained according to Examples 1 to 3 were dissolved in an equivalent quantity of NaOH/water or KOH/water.

Claims

1. Gemini surfactants of Formula (1)



wherein R¹ and R² stand for the radical of an aminocarboxylic acid, R³ for an alkyl radical having from 1 to 21 carbon atoms, and M for an alkali metal and/or alkaline earth metal, ammonium, alkyl ammonium, hydroxalkylammonium, and/or glucammonium, and wherein n may assume values from 1 to 20.

2. Surfactants according to claim 1, wherein n = 2.

3. Method for the production of compounds according to claim 2, wherein N,N'-ethylenediamine diacetate is reacted with a fatty acid derivative in aqueous medium in the presence of a base.

4. Method according to claim 3, wherein a fatty acid chloride is used as an acylating agent.

5. Method according to claims 3 and 4, wherein acetone and/or isopropanol is added to the reaction medium.

6. Method according to claims 3 to 5, wherein sodium, potassium and/or ammonium hydroxide are used as a base.

7. Method according to claims 3 to 6, wherein from 2 to 3 mol of fatty acid is used per mol of N,N'-ethylenediamine diacetate.

8. Method according to claims 3 to 7, wherein, following the acylation, a pH value of from 2 to 3 is established through addition of mineral acid.

9. Method according to claims 3 to 8, wherein the product obtained is neutralized with a base.

10. Use of the compounds according to claim 1 for the preparation of surface-active agents.

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Sehr geehrte Frau Anke Müller.

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